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RARE-EARTH ANALYSIS BY A MASS SPECTROMETRIC STABLE ISOTOPE DILUTION TECHNIQUE

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ABSTRACT

A technique for the analysis of rare-earth element abundances in rocks and minerals by mass spectrometric stable isotope dilution has been developed. The technique is being used at present for the routine analysis of europium and the seven even-atomic-number rare-earths; this is sufficient to clearly delineate the general rare-earth abundance pattern. The method yields results that are comparable, if not superior, in quality to those of neutron activation; it is also faster and simpler. Rare-earth abundances in the rock-standards W-1 and G-1 have been determined.

INTRODUCTION

Interest in the abundances of the geochemically sensitive rare-earth trace-elements has increased greatly during the past five years, primarily due to the application of neutron activation methods of analysis (Mosen et al., 1961; Haskin and Gehl, 1962; Towell et al., 1965). These techniques permit the accurate measurement of the rare-earth elements at the abundance levels found in natural materials. The emission and X-ray spectrographic methods of analysis previously used were neither sensitive nor accurate enough to give satisfactory determinations for many samples of interest. Standard neutron activation techniques, however, are time consuming and require the skills of an adept radiochemist. The purpose of this paper is to describe an entirely different method of rare-earth analysis which yields results that are comparable, if not superior, in quality to those of neutron activation, and which is both faster and simpler. This method is mass-spectrometric stable isotope dilution.

The isotope dilution method of analysis as used in geochemistry has been reviewed by Webster (1960) and a detailed description will not be given here. Basically, the method entails the determination of the concentration of a particular element by the change produced in its "natural" isotopic composition by the addition of a known amount of the element with abnormal isotopic composition. The added material with an enriched isotope is commonly termed the "spike."

Of the fourteen rare-earth elements that are found in meteorites and terrestrial rocks, ten have two or more isotopes and thus are amenable to isotope dilution analysis. Four of the rare-earths, Pr, Tb, Ho, and Tm, are monoisotopic and cannot be analyzed directly by this method.

ANALYTICAL PROCEDURE

The main steps in our procedure for rare-earth analysis are:

1. A composite rare-earth spike is added by pipet to a weighed powdered sample in a platinum dish. The composites consist of mixtures of the individual rare-earth element spikes combined in proportions that give near optimum spiking ratios for wide varieties of samples. We have been using 0.5 to 1 gram samples, in general, depending upon the expected concentrations of the rare-earths.
2. The sample is dissolved with HClO_4 and HF, in the case of silicates, and with HCl in the case of carbonates. Once the sample is in solution and the spike and sample have equilibrated, quantitative recovery is not necessary.
3. The rare-earth elements are concentrated by eluting the sample solution through a chromatographic column filled with Dowex 50W-X8, 200-400 mesh ion-exchange resin. The elution is performed with 2N HCl until strontium has come off the column, and then with 6N HCl to obtain the rare-earths. No attempt is made to separate the rare-earths cleanly from each other or from other elements with similar partition coefficients. However, the rare-earths are collected in two fractions, with Gd through Lu usually concentrated in one, and La through Eu in the other. These two fractions are subsequently analyzed separately in order to reduce the possibility of interference of the molecular oxide or chloride mass spectrum of the lighter (and generally more abundant) rare-earths with the elemental spectrum of the heavier rare-earths.
4. The particular fraction to be analyzed is evaporated to dryness, picked up in a drop of dilute HCl, and dried on two rhenium side-filaments of a standard

triple-filament, surface ionization, mass spectrometer source. The third, center, filament is also rhenium. The filaments are routinely degassed in an ion-pumped, bell-jar system and are checked for cleanliness in the mass spectrometer prior to loading of the sample.

5. The sample is analyzed on a CEC 21-703 mass-spectrometer (12 inch radius of curvature, 60° deflection) with a Faraday cup detector. The mass spectrum of the various rare-earth elements is scanned, usually one or two elements at a time, and concentrations are calculated from the measured isotope ratios. Eight scans of the appropriate mass region are usually sufficient for a good analysis. Stable ion currents of between 10^{-10} and 10^{-13} amps are routinely obtained from less than one microgram of most rare-earth elements. Singly-charged elemental species are used almost exclusively, rather than oxide, chloride, or multiply charged species. The concentration of an element is calculated from several pairs of isotopes, whenever possible, in order to check for interferences from various molecular species and for fractionation. Interference by molecular species can be detected ordinarily by changes in isotope ratios with time or with filament temperatures, due to differing volatilities of the species. Molecular interference, however, is rarely observed.

ADDITIONAL CONSIDERATIONS

This procedure was a natural outgrowth of the similar method that is used routinely in our laboratory for Rb-Sr geochronology. Because the method yields stable ion-currents with no significant interferences over long periods of time, we have not attempted an extensive study of separation or mass spectrometric procedures. Our method, therefore, may not be the optimum. It does,

however, give quite satisfactory results. The method also permits the routine determination of a large number of elements other than the rare-earths, from the same sample, simply by collecting different column fractions.

Spikes for the 10 polyisotopic rare-earths were purchased from the Oak Ridge National Laboratory. With exceptions in the case of La and Lu, the concentration of each of the enriched isotopes was approximately 90% or more. Isotopic compositions of the spikes were measured by mass spectrometric analysis; discrepancies between our values and those reported by Oak Ridge were less than 0.5% in all cases. The concentrations of the spikes were determined by calibration with "spec-pure" rare-earth salts of normal isotopic composition that were purchased from Johnson-Matthey and Company, Ltd. London, and from the American Potash and Chemical Corporation, Rare Earth (Lindsay) Division, Chicago. The calibration was performed by mass spectrometric analysis of a mixture of a measured amount of the spike and a measured amount of the normal "Spec-pure" rare-earth of known concentration. Determined concentrations were, in all cases, in good agreement with those calculated from the weight of the powdered spike as received from Oak Ridge and the dilution factor used in making up the liquid spike. Composite rare-earth spike solutions were made from the individual spikes and these are used in the routine analyses.

Purified reagents are used throughout the chemical procedure, with the exception of reagent A. C. S. grade hydrofluoric acid. Contamination was determined by putting the rare-earth spike through the complete chemical and mass-spectrometric procedure. The Ce blank was approximately 0.1μ gm; the other rare-earth blanks were less than 0.01μ gm.

We routinely analyze eight of the ten polyisotopic rare-earth elements. Lu and La are not analyzed presently because of analytical difficulties. The Lu spike is enriched in Lu^{176} ; this isotope has isobaric Yb and Hf interferences. In addition, Lu does not emit strongly from the rhenium triple filament source. It is possible, however, to obtain fairly satisfactory results for Lu by making corrections for the interfering elements. On the other hand, the interference problems for La are much more severe. The enriched La isotope, mass 138, is isobaric with the main isotope of barium, and a minor isotope of Ce. Both Ba and Ce are ordinarily more abundant in rocks than La. Both are eluted from the columns, in our procedure, in the same fraction as La. Preliminary work with ethyl-alcohol solvent-extraction indicates that Ba can be cleanly separated from the rare-earths. It is possible to analyze La in the same fraction as Ce because of the greater sensitivity of LaO^+ than CeO^+ in the mass spectrometer, if the source region is kept at high pressure, about 10^{-5} torr (A. Masuda, personal communication, 1967). However, the greatest available enrichment of the La-138 isotope is approximately 2.2% abundance (compared to 0.09% in normal La). Thus any contribution by Ba or Ce to this mass will seriously affect the analysis. Until more enriched La spikes are available, La cannot be determined with the accuracy and precision of the other polyisotopic rare-earths. The failure to give high quality La determinations would seem to be the weakest point of our present procedure for rare-earth analysis. Otherwise, we believe that the rare-earth abundance patterns of rocks and minerals are accurately and adequately described, essentially over the entire mass range, by our determinations of Eu and the seven even-atomic-number rare-earths.

It was hoped, initially, that the sensitivity of adjacent rare-earth elements

in the thermal ionization process might be similar or vary in a linear fashion so that the abundances of the rare-earths that cannot be determined by isotope dilution might be determined by extrapolation from the calculated abundances of the other rare-earths. This, however, is not possible, inasmuch as the relative emission of adjacent rare-earths cannot be predictably controlled to an adequate accuracy ($<10\%$) for any appreciable length of time. The selective filament emission, however, is useful in that it permits the collection of data for a particular element while interfering elements are emitting weakly. It is particularly useful in the analysis for Ce and for Lu inasmuch as these elements do not have isotope pairs that are free from isobaric interference.

ANALYSES OF G-1 AND W-1

Independent duplicate analyses of the standard diabase W-1 and of the standard granite G-1 were made by the isotope dilution technique. The averages are given in Table 1. The errors shown are not standard deviations but rather the (maximum) deviation of the analyses from the average values. The errors for W-1 are less than 1%. The errors for G-1 are in general larger, and for Nd and Sm they are a good deal larger than would be expected from the internal precision of the individual analyses. These errors were not reduced by a third analysis for Nd and Sm. We can give no analytical explanation for the larger deviations found for these elements in G-1.

The results of analyses for the same rare-earths in W-1 and G-1 by Haskin and Gehl (1963) and Towell *et al.* (1965) are also given in Table 1. Both groups used neutron activation techniques which differed primarily in the fact that the former group did post-irradiation chemical separations whereas the latter

group did pre-irradiation chemistry. The errors given with the neutron activation data are the reported standard deviations. A summary of rare-earth abundances in G-1 and W-1 as determined by a number of methods, is given in Fleischer (1965).

There is excellent agreement between our rare-earth analyses of W-1 and those of Haskin and Gehl. Agreement with the analyses of Towell, et al. is much poorer. For G-1, our values are in closer agreement with those of Towell, et al. than with those of Haskin and Gehl. Differences between our duplicate analyses (triplicate for Nd and Sm) of G-1 are larger for many of the rare-earths than expected from the internal precision, (the standard deviation of the mean of a number of determinations, each determination being calculated from two scans). We have found the same situation for three independent determinations of barium in G-1 (Schnetzler, et al., 1967). This lack of agreement within a laboratory and between laboratories may be a manifestation of heterogeneous distribution of rare-earth (and barium) bearing phases within and between bottles of G-1, as suggested by Haskin and Gehl.

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Table 1
Rare-earths in W-1 & G-1, ppm by weight

	W-1			G-1		
	This work	Haskin and Gehl (1963)	Towell, et al. (1965)	This work	Haskin and Gehl (1963)	Towell, et al. (1965)
Ce	23.6 ± 0.1	24.3 ± 0.24	15.1 ± 2.4	173. ± 1	134. ± 13	150. ± 24
Nd	15.04 ± 0.07	15.1 ± 1.4	20.2 ± 2.0	66.4 ± 2.4	54.6 ± 1.5	55.2 ± 5.5
Sm	3.76 ± 0.01	3.79 ± 0.32	3.46 ± 0.03	8.89 ± 0.30	8.6 ± 0.56	8.25 ± 0.08
Eu	1.126 ± 0.003	1.09 ± 0.12	1.29 ± 0.05	1.24 ± 0.01	1.04 ± 0.11	1.36 ± 0.05
Gd	4.03 ± 0.04	4.2 ± 0.35	-----	4.58 ± 0.01	4.88 ± 0.13	-----
Dy	4.01 ± 0.02	-----	4.38 ± 0.18	2.52 ± 0.05	-----	2.52 ± 0.10
Er	2.35 ± 0.03	2.57 ± 0.26	-----	0.969 ± 0.002	1.40 ± 0.14	-----
Yb	2.09 ± 0.02	2.10 ± 0.01	2.23 ± 0.18	0.862 ± 0.019	0.625 ± 0.06	0.937 ± 0.075